

# Density functional formulation of the Random Phase Approximation for inhomogeneous fluids: application to the Gaussian core and Coulomb particles

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Using the adiabatic connection, we formulate the free energy in terms of the correlation function of a fictitious system,  $h_\lambda(\mathbf{r}, \mathbf{r}')$ , where  $\lambda$  determines the interaction strength. To obtain  $h_\lambda(\mathbf{r}, \mathbf{r}')$  we use the Ornstein-Zernike equation, and the two equations constitute a general liquid-state framework for treating inhomogeneous fluids. As the two equations do not form a closed set, an approximate closure relation is required and it determines a type of an approximation. In the present work we investigate the random phase approximation (RPA) closure. We determine that this approximation is identical to the variational Gaussian approximation derived within the framework of the field-theory. We then apply our generalized RPA approximation to the Gaussian core model and Coulomb charges.

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## I. INTRODUCTION

Pair interactions of hard-sphere fluids derive from the excluded volume effects: non-overlapping configurations recover an ideal-gas behavior, but the exclusion of overlapping configurations reduces available phase-space, leading at high density to phase transition. In this sense the hard-sphere fluids constitute a geometric problem. Within various successful (nonlocal) density functional theories (DFT), a free energy functional for hard-sphere fluids is built from a weighted rather than local density — non-locality is attained by construction [1]. In early prescriptions, a weighted density corresponded to a convoluted local density, where the single convoluting function was the Mayer f-function. The resulting theories, their refinements and extensions came to be known as the weighted DFT theories. A crucial next development was to decompose a Mayer f-function into several weight functions, yielding multiple weighted densities and, by the same token, multiple building blocks from which an approximate  $F_{\text{ex}}$  was to be constructed [2–6]. Referred to as the fundamental measure (FM) DFT, a nice feature of this approach is the capture of a correct dimensional crossover: each consecutive reduction of the system dimensionality,  $3\text{D} \rightarrow 2\text{D} \rightarrow 1\text{D} \rightarrow 0\text{D}$ , recovers either an accurate or exact  $F_{\text{ex}}$ .

The success of the hard-sphere DFT theories (and the lack of equivalent theories for arbitrary pair interactions), prompted attempts to implement the hard-sphere framework to other types of short-range interactions. It became something of a standard method to map particles with arbitrary short-range interactions onto a hard-sphere fluid by ascribing to a pair potential of interest an effective diameter. Density profiles are then obtained from the DFT theories for hard-spheres. The Barker-Henderson effective diameter is one recipe among others

for extracting an effective diameter [7].

A more sophisticated example is the “soft” fundamental measure DFT developed for penetrable spheres (spheres may overlap but at an energy cost). Within this method  $F_{\text{ex}}$  is constructed to satisfy a correct dimensional crossover [8–12].

But for particles with arbitrary pair interactions, where excluded volume effects are not dominant, the mean-field approximation is still a preferred theoretical tool [13–17]. An obvious example are charged particles with long-range interactions. Other examples are particles with bound (non-divergent) interactions, known as penetrable particles. This class includes the Gaussian core model, or the already mentioned penetrable spheres. But the correlations neglected by the mean-field description are not always trivial. This is particularly true of Coulomb systems. In such a case the “beyond-mean-field” approach is desirable. Splitting the excess free energy into the mean-field and correlation contribution,  $F_{\text{ex}}[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') + F_c[\rho]$ , where  $\rho(\mathbf{r})$  is a number density, and  $u(\mathbf{r}, \mathbf{r}')$  is an arbitrary pair interaction, the “beyond-mean-field” approach amounts to finding an appropriate functional  $F_c[\rho]$ .

The “beyond-mean-field” approximations for Coulomb systems are dominantly formulated within the field-theoretical framework based on mathematical transformation of a partition function, using a Gaussian integral identity [18], into a functional integral over an auxiliary fluctuating field [18–26]. The saddle-point of the effective Hamiltonian recovers the mean-field solution, while the harmonic fluctuations around the saddle-point account for weak (Gaussian) correlations. If formulated variationally, the equations become self-consistent (non-perturbative) and generally are deemed superior to the perturbative formulation [18, 23, 24].

A drawback of the field-theoretical formulation is the

loss of physical intuition after one moves from physical to auxiliary phase-space. In the present work we re-derive the variational Gaussian equations of the field-theoretical framework using only the liquid-state theory. The Gaussian approximation is equivalent to the well established random phase approximation (RPA) [27], a mathematical signature of which is its being comprised of an infinite summation of ring diagrams [28]. Our formulation of the RPA is general and in principle applicable to any pair interactions. We apply our generalized RPA approximation to the Gaussian core model, considered to be a weakly correlated fluid [13], a one-component plasma, and finally a symmetric electrolyte.

In Sec. II we formulate the free energy within the liquid-state formalism using the adiabatic connection. By coupling it to the OZ equation, we set up a general theoretical framework for inhomogeneous fluids. In Sec. III we consider the RPA closure and derive the appropriate self-consistent equations. In Sec. IV we generalize the equations to multiple species. Finally, in Secs. V, VI, and VII we test the RPA approximation on concrete systems with wall geometry.

## II. ADIABATIC CONNECTION FORMULATION OF THE FREE ENERGY

Given a general Hamiltonian for a system of interacting particles,

$$H = \sum_{i=1}^N U(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^N u(\mathbf{r}_i, \mathbf{r}_j), \quad (1)$$

where  $U(\mathbf{r})$  is an external potential,  $u(\mathbf{r}, \mathbf{r}')$  is a pair interaction, and  $N$  is the number of particles, our aim is to obtain a free energy expression in terms of physically meaningful quantities. To this end we use the adiabatic connection route [29, 30], wherein interactions are gradually switched on within a fictitious  $\lambda$ -dependent system,

$$H_\lambda = \sum_{i=1}^N U_\lambda(\mathbf{r}_i) + \frac{\lambda}{2} \sum_{i \neq j}^N u(\mathbf{r}_i, \mathbf{r}_j), \quad (2)$$

where the  $\lambda$ -dependent external potential  $U_\lambda(\mathbf{r})$  is introduced to keep a density fixed at its physical value for all  $\lambda$ , and  $\lambda = 1$  recovers the physical potential,  $U_{\lambda=1}(\mathbf{r}) = U(\mathbf{r})$ .

The partition function and the free energy of a fictitious system are

$$Z_\lambda = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N e^{-\beta H_\lambda} \quad (3)$$

and

$$\beta F_\lambda = -\log Z_\lambda, \quad (4)$$

respectively. The free energy of a physical system can be expressed in terms of a fictitious system, as a thermodynamic integration,

$$F = F_0 + \int_0^1 d\lambda \frac{\partial F_\lambda}{\partial \lambda}, \quad (5)$$

where the reference free energy is

$$F_0[\rho] = F_{\text{id}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) U_{\lambda=0}(\mathbf{r}), \quad (6)$$

and

$$F_{\text{id}}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\log \rho(\mathbf{r}) \Lambda^3 - 1] \quad (7)$$

is an ideal-gas free energy. The integrand in Eq. (5) can be written as

$$\begin{aligned} \frac{\partial F_\lambda}{\partial \lambda} &= \int d\mathbf{r} \rho(\mathbf{r}) \frac{\partial U_\lambda(\mathbf{r})}{\partial \lambda} \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') h_\lambda(\mathbf{r}, \mathbf{r}') u(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (8)$$

and Eq. (5) becomes

$$\begin{aligned} F[\rho] &= F_{\text{id}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) U_{\lambda=0}(\mathbf{r}) \\ &+ \int_0^1 d\lambda \int d\mathbf{r} \rho(\mathbf{r}) \frac{\partial U_\lambda(\mathbf{r})}{\partial \lambda} \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \int_0^1 d\lambda h_\lambda(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (9)$$

Then after a few cancelations we arrive at the final form,

$$\begin{aligned} F[\rho] &= F_{\text{id}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) U(\mathbf{r}) \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \int_0^1 d\lambda h_\lambda(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (10)$$

Note that the final expression does not depend on the fictitious potential  $U_\lambda$ . The only quantity that depends on  $\lambda$  is a correlation function  $h_\lambda(\mathbf{r}, \mathbf{r}')$ . The last line of the expression represents the correlation free energy,

$$F_c[\rho] = \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} \rho(\mathbf{r}) \left[ \int d\mathbf{r}' \rho(\mathbf{r}') h_\lambda(\mathbf{r}, \mathbf{r}') u(\mathbf{r}, \mathbf{r}') \right]. \quad (11)$$

Not surprisingly,  $F_c$  depends on the correlation function,  $h_\lambda(\mathbf{r}, \mathbf{r}')$ , that is obtained from the Ornstein-Zernike equation (OZ),

$$h_\lambda(\mathbf{r}, \mathbf{r}') = c_\lambda(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' \rho(\mathbf{r}'') h_\lambda(\mathbf{r}', \mathbf{r}'') c_\lambda(\mathbf{r}, \mathbf{r}''), \quad (12)$$

which is a well known exact relation within the liquid-state theory. Because the direct correlation function  $c_\lambda(\mathbf{r}, \mathbf{r}')$  is not known, an appropriate closure relation is still required.

### III. RANDOM PHASE APPROXIMATION

We consider the simplest closure available,

$$c_\lambda(\mathbf{r}, \mathbf{r}') = -\beta\lambda u(\mathbf{r}, \mathbf{r}'), \quad (13)$$

known as the random phase approximation (RPA). The closure modifies the exact Ornstein-Zernike relation in Eq. (12),

$$\begin{aligned} h_\lambda(\mathbf{r}, \mathbf{r}') &= -\beta\lambda u(\mathbf{r}, \mathbf{r}') \\ &- \beta\lambda \int d\mathbf{r}'' \rho(\mathbf{r}'') h_\lambda(\mathbf{r}', \mathbf{r}'') u(\mathbf{r}, \mathbf{r}''). \end{aligned} \quad (14)$$

Accordingly, we refer to it as the OZ-RPA equation. Application of the OZ-RPA modifies the correlation free energy in Eq. (11),

$$F_c[\rho] = -\frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int_0^1 d\lambda \frac{h_\lambda(\mathbf{r}, \mathbf{r})}{\lambda\beta} - \frac{u(0)}{2} \int d\mathbf{r} \rho(\mathbf{r}). \quad (15)$$

In the above equation  $u(0) = u(\mathbf{r}, \mathbf{r})$ . Likewise, for a homogeneous fluids in a bulk we write  $h_b(0) = h_b(\mathbf{r}, \mathbf{r})$ .

#### A. Connection with the field-theoretical formulation

The  $\lambda$ -dependence in  $F_c$  can be eliminated by expanding  $h_\lambda(\mathbf{r}, \mathbf{r}')$ ,

$$\begin{aligned} h_\lambda(\mathbf{r}, \mathbf{r}') &= -\beta\lambda u(\mathbf{r}, \mathbf{r}') \\ &+ \beta^2 \lambda^2 \int d\mathbf{r}_1 \rho(\mathbf{r}_1) u(\mathbf{r}, \mathbf{r}_1) u(\mathbf{r}_1, \mathbf{r}') \\ &- \beta^3 \lambda^3 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) u(\mathbf{r}, \mathbf{r}_1) u(\mathbf{r}_1, \mathbf{r}_2) u(\mathbf{r}_2, \mathbf{r}') \\ &+ \dots \end{aligned} \quad (16)$$

The expansion is generated iteratively by repeated insertion of the right hand side of Eq. (14) for every occurrence of  $h_\lambda(\mathbf{r}, \mathbf{r}')$ . The notation is simplified by introducing an operator

$$A(\mathbf{r}, \mathbf{r}') = \beta\rho(\mathbf{r})u(\mathbf{r}, \mathbf{r}'), \quad (17)$$

and adopting a convention

$$A^n = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \dots \int d\mathbf{r}_{n-1} A(\mathbf{r}, \mathbf{r}_1) A(\mathbf{r}_1, \mathbf{r}_2) \dots A(\mathbf{r}_{n-1}, \mathbf{r}') \quad (18)$$

by means of which we get

$$\begin{aligned} \rho(\mathbf{r}) h_\lambda(\mathbf{r}, \mathbf{r}') &= -\lambda A + \lambda^2 A^2 - \lambda^3 A^3 + \dots \\ &= -\left( \frac{\lambda A}{I + \lambda A} \right), \end{aligned} \quad (19)$$

where  $I = \delta(\mathbf{r}, \mathbf{r}')$  is the identity matrix in the continuum limit. Integration over  $\lambda$  now is done explicitly,

$$\int_0^1 d\lambda \frac{\rho(\mathbf{r}) h_\lambda(\mathbf{r}, \mathbf{r}')}{\lambda} = -A + \frac{A^2}{2} - \frac{A^3}{3} + \dots = -\log[I + A], \quad (20)$$

and  $F_c[\rho]$  becomes

$$F_c[\rho] = \frac{k_B T}{2} \text{Tr} \log[I + A] - \frac{u(0)}{2} \int d\mathbf{r} \rho(\mathbf{r}), \quad (21)$$

where the first term yields an infinite series of ring diagrams, a characteristic feature of the RPA.

The expression can further be rearranged by using the formal matrix identity,

$$\frac{1}{2} \text{Tr} \log[I + A] = \log \sqrt{\det[I + A]}, \quad (22)$$

and the fact that a functional determinant is a solution of a Gaussian functional integral,

$$\frac{1}{\sqrt{\det[I + A]}} = \int \mathcal{D}\phi e^{-\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) \phi(\mathbf{r}') [\delta(\mathbf{r} - \mathbf{r}') + A(\mathbf{r}, \mathbf{r}')]}, \quad (23)$$

where  $\phi(\mathbf{r})$  is a fluctuating field and  $\int \mathcal{D}\phi$  is a functional integral. The partition function within the RPA can now be written as a Gaussian functional integral,

$$\begin{aligned} Z_{\text{rpa}} &= e^{\frac{\beta N}{2} u(0)} e^{-\beta F_{\text{mf}}} \\ &\times \int \mathcal{D}\phi e^{-\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) \phi(\mathbf{r}') [\delta(\mathbf{r} - \mathbf{r}') + A(\mathbf{r}, \mathbf{r}')]}, \end{aligned} \quad (24)$$

where we used  $F = F_{\text{mf}} + F_c$  and  $Z = e^{-\beta F_{\text{mf}}} e^{-\beta F_c}$ . The functional integral formulation has been recovered without resorting to the Hubbard-Stratonovich transformation, starting from the liquid-state formulation.

#### B. density profile

To obtain an equilibrium density we use the known thermodynamic condition,

$$\frac{\delta F}{\delta \rho(\mathbf{r})} = \mu, \quad (25)$$

where  $\mu$  denotes the chemical potential. The functional derivative of  $F_c$  with respect to  $\rho(\mathbf{r})$  incidentally eliminates all  $\lambda$ -dependence,

$$\begin{aligned}\frac{\delta F_c}{\delta \rho(\mathbf{r})} &= \frac{k_B T}{2} \frac{\delta \text{Tr} \log [I + A]}{\delta \rho(\mathbf{r})} - \frac{1}{2} u(0) \\ &= -\frac{1}{2} \left[ u(0) + k_B T h(\mathbf{r}, \mathbf{r}) \right],\end{aligned}\quad (26)$$

and the functional derivative is written in terms of a correlation function of a physical system,  $h(\mathbf{r}, \mathbf{r})$ . The number density that results is

$$\rho(\mathbf{r}) = \rho_b e^{-\beta U(\mathbf{r})} e^{-\beta \int d\mathbf{r}' \rho(\mathbf{r}') u(\mathbf{r}, \mathbf{r}')} e^{\frac{1}{2} [\beta u(0) + h(\mathbf{r}, \mathbf{r})] + \beta \mu_{\text{ex}}}, \quad (27)$$

where we separated a chemical potential into ideal and excess parts,  $\mu = \mu_{\text{id}} + \mu_{\text{ex}}$ , with the ideal contribution related to a bulk density,

$$\rho_b = \left( \frac{e^{\beta \mu_{\text{id}}}}{\Lambda^3} \right). \quad (28)$$

The excess chemical potential within the present approximation is

$$\mu_{\text{ex}} = \rho_b \int d\mathbf{r} u(r) - \frac{1}{2} [u(0) + k_B T h_b(0)], \quad (29)$$

where  $h_b(r)$  is a correlation function in a bulk. For  $U(\mathbf{r}) = 0$ , we accurately recover a bulk density,  $\rho(\mathbf{r}) \rightarrow \rho_b$ . More conveniently, a density can be written as

$$\rho(\mathbf{r}) = \rho_b e^{-\beta U(\mathbf{r})} e^{-\beta \int d\mathbf{r}' (\rho(\mathbf{r}') - \rho_b) u(\mathbf{r}, \mathbf{r}')} e^{\frac{1}{2} [h(\mathbf{r}, \mathbf{r}) - h_b(0)]}. \quad (30)$$

### C. pressure

Another quantity of interest is pressure that can be obtained from a type of thermodynamic integration involving a chemical potential,

$$P_{\text{ex}} = \int_0^{\rho_b} d\rho \rho \frac{\partial \mu_{\text{ex}}}{\partial \rho}, \quad (31)$$

where  $P = k_B T \rho_b + P_{\text{ex}}$ . The resulting expression shows  $\lambda$ -dependence,

$$P_{\text{ex}} = \frac{1}{2} \rho_b^2 \int d\mathbf{r} u(r) - \frac{k_B T}{2} \rho_b \left[ h_b(0) - \int_0^1 d\lambda \frac{h_{b,\lambda}(0)}{\lambda} \right]. \quad (32)$$

## IV. MULTIPLE SPECIES

We next generalize the RPA to multiple species. The fictitious Hamiltonian, equivalent to that in Eq. (2), is

$$H_\lambda = \sum_{i=1}^N U_i^\lambda(\mathbf{r}_i) + \frac{\lambda}{2} \sum_{i \neq j}^N u_{ij}(\mathbf{r}_i, \mathbf{r}_j). \quad (33)$$

Here we assume that each particle feels different external potential, and pair interactions between different pairs are different. Of course, particles are not all different but are grouped into species.

Assuming  $K$  different species, the free energy from adiabatic connection is

$$\begin{aligned}F[\{\rho_k\}] &= F_{\text{id}}[\{\rho_k\}] + \sum_{k=1}^K \int d\mathbf{r} U_k(\mathbf{r}) \rho_k(\mathbf{r}) \\ &+ \frac{1}{2} \sum_{k,l}^K \int d\mathbf{r} \int d\mathbf{r}' \rho_k(\mathbf{r}) \rho_l(\mathbf{r}') u_{kl}(\mathbf{r}, \mathbf{r}') \\ &+ \frac{1}{2} \sum_{k,l}^K \int d\mathbf{r} \int d\mathbf{r}' \rho_k(\mathbf{r}) \rho_l(\mathbf{r}') u_{kl}(\mathbf{r}, \mathbf{r}') \int_0^1 d\lambda h_{kl}^\lambda(\mathbf{r}, \mathbf{r}'),\end{aligned}\quad (34)$$

where the ideal-gas contribution is

$$\beta F_{\text{id}}[\{\rho_k\}] = \sum_{i=1}^K \int d\mathbf{r} \rho_k(\mathbf{r}) \left[ \log \rho_k(\mathbf{r}) \Lambda^3 - 1 \right]. \quad (35)$$

If the Ornstein-Zernike equation for multiple-species is

$$h_{kl}^\lambda(\mathbf{r}, \mathbf{r}') = c_{kl}^\lambda(\mathbf{r}, \mathbf{r}') + \sum_{n=1}^K \int d\mathbf{r}'' \rho_n(\mathbf{r}'') h_{nl}^\lambda(\mathbf{r}', \mathbf{r}'') c_{kn}^\lambda(\mathbf{r}'', \mathbf{r}), \quad (36)$$

where correlations between particles of a species  $k$  and  $l$  are mediated by all particles disregarding their type, then the RPA closure,  $c_{kl}^\lambda = \beta \lambda u_{kl}(\mathbf{r}, \mathbf{r}')$ , yields

$$\begin{aligned}h_{kl}^\lambda(\mathbf{r}, \mathbf{r}') &= -\beta \lambda u_{kl}(\mathbf{r}, \mathbf{r}') \\ &- \beta \lambda \sum_n \int d\mathbf{r}'' \rho_n(\mathbf{r}'') h_{nl}^\lambda(\mathbf{r}', \mathbf{r}'') u_{kn}(\mathbf{r}'', \mathbf{r}),\end{aligned}\quad (37)$$

and the RPA correlation free energy is

$$\begin{aligned}F_c^{\text{rpa}} &= -\frac{1}{2} \sum_{k=1}^K u_{kk}(0) \int d\mathbf{r} \rho_k(\mathbf{r}) \\ &- \frac{1}{2} \sum_{k=1}^K \int d\mathbf{r} \rho_k(\mathbf{r}) \int_0^1 d\lambda \frac{h_{kk}^\lambda(\mathbf{r}, \mathbf{r})}{\beta \lambda}.\end{aligned}\quad (38)$$

(Compare with Eq. (15) for a one component system). The lack of dependence on inter-species correlations, that is,  $h_{kl}(\mathbf{r}, \mathbf{r}')$  for  $k \neq l$ , at first glance appears inaccurate. But as correlations between particles of the same species,  $h_{kk}(\mathbf{r}, \mathbf{r}')$ , are mediated by all the particles disregarding their type, the cross-correlations are always implicit in  $h_{kk}(\mathbf{r}, \mathbf{r}')$ .

### A. density

An equilibrium density of a species  $k$  is obtained from the condition

$$\frac{\delta F}{\delta \rho_k(\mathbf{r})} = \mu_k, \quad (39)$$

and the correlational counterpart yields

$$\frac{\delta F_c}{\delta \rho_k(\mathbf{r})} = -\frac{u_{kk}(0)}{2} - \frac{k_B T}{2} h_{kk}(\mathbf{r}, \mathbf{r}). \quad (40)$$

If the excess chemical potential of a specie  $k$  is

$$\mu_k^{\text{ex}} = \sum_l^K \rho_l^b \int d\mathbf{r} u_{kl}(r) - \frac{1}{2} \left[ u_{kk}(0) + k_B T h_{kk}^b(0) \right], \quad (41)$$

then a density is

$$\begin{aligned} \rho_k(\mathbf{r}) &= \rho_k^b e^{-\beta U_k(\mathbf{r})} e^{-\beta \sum_{l=1}^K \int d\mathbf{r}' (\rho_l(\mathbf{r}') - \rho_l^b) u_{kl}(\mathbf{r}, \mathbf{r}')} \\ &\times e^{\frac{1}{2} [h_{kk}(\mathbf{r}, \mathbf{r}) - h_{kk}^b(0)]}. \end{aligned} \quad (42)$$

## B. pressure

To obtain the pressure we use  $P_{\text{ex}} = \sum_{k=1}^K \rho_k^b \mu_k^{\text{ex}} - f_{\text{ex}}$ , where the excess free energy density in a bulk is

$$\begin{aligned} f_{\text{ex}} &= \frac{1}{2} \sum_{k,l}^K \rho_k^b \rho_l^b \int d\mathbf{r} u_{kl}(r) \\ &- \frac{1}{2} \sum_{k=1}^K \rho_k^b \left[ u_{kk}(0) + k_B T \int_0^1 d\lambda \frac{h_{kk}^{b,\lambda}(0)}{\lambda} \right]. \end{aligned} \quad (43)$$

The excess pressure then becomes

$$\begin{aligned} P_{\text{ex}} &= \frac{1}{2} \sum_{k,l}^K \rho_k^b \rho_l^b \int d\mathbf{r} u_{kl}(r) \\ &- \frac{k_B T}{2} \sum_{k=1}^K \rho_k^b \left[ h_{kk}(0) - \int_0^1 d\lambda \frac{h_{kk}^{b,\lambda}(0)}{\lambda} \right]. \end{aligned} \quad (44)$$

## V. THE GAUSSIAN CORE MODEL (GCM)

We apply the developed RPA approximation to the Gaussian core model (GCM), whose pair interactions have the Gaussian functional form,

$$\beta u(r) = \varepsilon e^{-r^2/\sigma^2}. \quad (45)$$

$\sigma$  is the length scale that determines the interaction range and  $\varepsilon$  determines the interaction strength. Because the potential is bound, the GCM particles are said to be penetrable.

For a homogenous system the free energy in Eq. (21) can be calculated exactly, and each individual ring term becomes

$$\text{Tr } A^n = \frac{V(\varepsilon \eta_b)^n}{(n\pi\sigma^2)^{3/2}} \quad (46)$$

where  $\eta_b = \pi^{3/2} \sigma^3 \rho_b$  is the reduced density and  $V$  is the volume of a system. The correlation free energy density,  $f_c = F_c/V$ , becomes

$$\begin{aligned} f_c &= \frac{\varepsilon \rho_b}{2} \sum_{n=2}^{\infty} \frac{(-\varepsilon \eta)^{n-1}}{n^{5/2}} \\ &= -\frac{\varepsilon \rho_b}{2} \left\{ 1 + \frac{\text{Li}_{5/2}[-\varepsilon \eta]}{\varepsilon \eta} \right\}, \end{aligned} \quad (47)$$

where  $\text{Li}_m(x) = \sum_{n=1}^{\infty} \frac{x^n}{n^m}$  is a polylogarithm. We may now obtain any quantity of interest. For example, the excess chemical potential is

$$\beta \mu_{\text{ex}} = \varepsilon \eta - \frac{\varepsilon}{2} \left\{ 1 + \frac{\text{Li}_{3/2}[-\varepsilon \eta]}{\varepsilon \eta} \right\} \quad (48)$$

Comparing with Eq. (29) we get another useful quantity,

$$h_b(0) = \varepsilon \sum_{n=1}^{\infty} \frac{(-1)^n (\varepsilon \eta)^{n-1}}{n^{3/2}}, \quad (49)$$

and the pressure is written as

$$\frac{\beta P_{\text{ex}}}{\rho_b} = \frac{\varepsilon}{2} \left\{ \eta + \frac{\text{Li}_{5/2}(-\varepsilon \eta) - \text{Li}_{3/2}(-\varepsilon \eta)}{\varepsilon \eta} \right\}. \quad (50)$$

Our primary interest, however, lies in the RPA as a theory of inhomogeneous fluids. Considering a fluid confined by a hard wall at  $x = 0$  to a half space  $x > 0$ , we can use the contact value theorem to predict the density at a contact with a wall from a bulk pressure,

$$\begin{aligned} \rho(0) &= \beta P \\ &= \rho_b \left[ 1 + \frac{\varepsilon \eta}{2} + \frac{\text{Li}_{5/2}(-\varepsilon \eta) - \text{Li}_{3/2}(-\varepsilon \eta)}{2\eta} \right]. \end{aligned} \quad (51)$$

The first term is the ideal-gas contribution, the second is the mean-field contribution, and the last term accounts for the RPA correlations.

In Fig. (1) we compare the contact density at a wall as a function of  $\varepsilon$  for different approximations. The RPA correlations lower the mean-field predictions, and the RPA corrections become more accurate at high densities, that is, for a larger number of overlaps.

In Fig. (2) we plot the entire density profiles near a planar wall at  $x = 0$ . The mean-field is not expected to be accurate for  $\varepsilon > 1$  and the largest deviations from the exact results occur near the wall. The RPA profile not only improves the contact region but an entire profile, even for as large values of the interaction strength as  $\varepsilon = 7$ .

To complete the analysis, we consider next a two component GCM system with interactions

$$u_{ij}(x) = \begin{cases} \varepsilon e^{-r^2/\sigma^2}, & \text{if } i = j \\ -\varepsilon e^{-r^2/\sigma^2}, & \text{if } i \neq j. \end{cases}$$

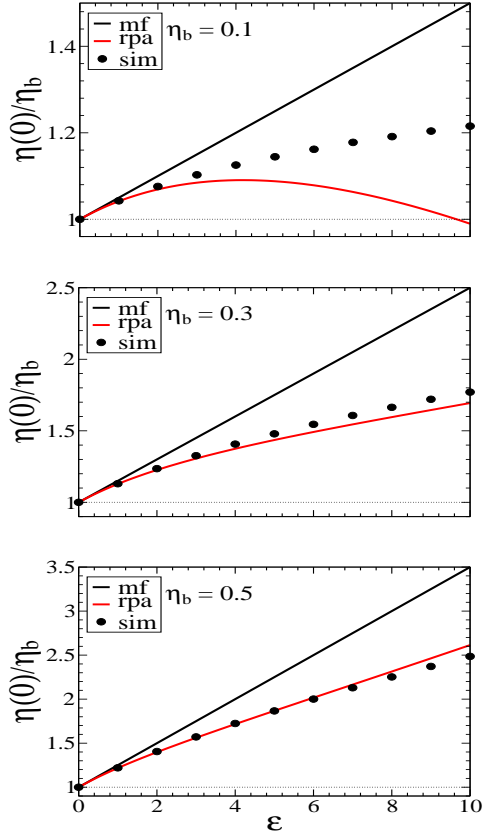


FIG. 1: The contact density,  $\eta(0) = \pi^{3/2}\sigma^3\rho(0)$ , as a function of an interaction strength  $\varepsilon$  for a one component GCM.  $\eta_b$  is the bulk reduced density. The dotted horizontal line corresponds to an ideal-gas prediction.

The bulk density of both species is the same,  $\rho_b = \rho_b^+ = \rho_b^-$ , so that the mean-field contributions are canceled out and the density profile is determined strictly by correlations. In Fig. (3) we compare a density profile of the RPA approximation with that from the simulation. The depletion of particles from the interface region is caused by unfavorable energy cost when a particle is removed from a bulk, which requires breaking of various "bonds" with its neighbors.

## VI. ONE-COMPONENT PLASMA

We consider next Coulomb particles and transform the previously obtained expressions of the RPA approximation to more familiar expressions in terms of an electrostatic potential. The resulting expressions are the same as those obtained for a variational Gaussian approximation within the field-theoretical framework [23, 24] and without resorting to the Hubbard-Stratonovich transformation.

Coulomb charges  $q$  interact via the following pair po-

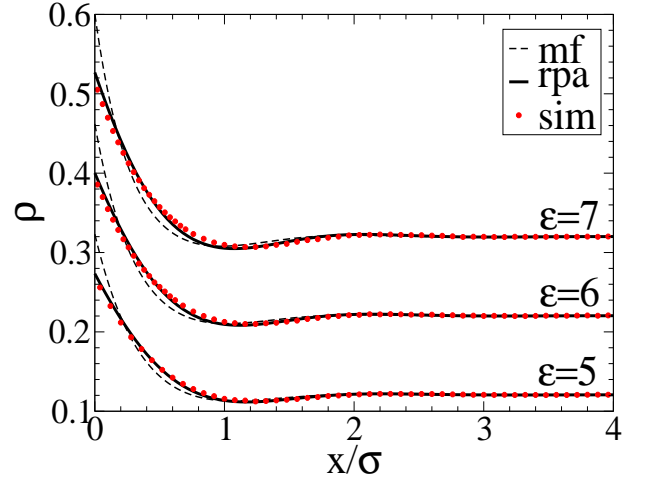


FIG. 2: Density profile for the GCM near a planar wall for different values of the interaction strength:  $\varepsilon = 5, 6, 7$ . A simulation box dimensions are  $20\sigma : 20\sigma : 20\sigma$  and it contains 1000 particles. Without hard wall constraint this corresponds to a bulk reduced density  $\eta_b \approx 0.7$ . The numerical data points for the mean-field and the RPA correspond to the same conditions.

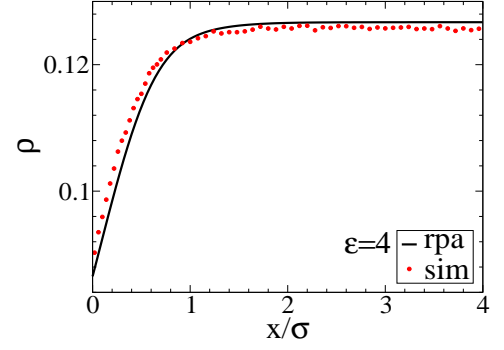


FIG. 3: The total density profile near a planar wall for the two component GCM fluid, for  $\varepsilon = 4$ . The system size and the number of particles is the same as in Fig. (2), except the total density is made up of two species which have identical density profiles. The density is determined by correlations alone as the mean-field effects cancel out.

tential,

$$u(\mathbf{r}, \mathbf{r}') = \frac{q^2}{4\pi\epsilon|\mathbf{r} - \mathbf{r}'|}, \quad (52)$$

where  $\epsilon$  is the background dielectric constant. A number density of Coulomb charges, using Eq. (30), is

$$\rho(\mathbf{r}) = \rho_b e^{-\beta q\psi(\mathbf{r})} e^{\frac{1}{2}[h(\mathbf{r}, \mathbf{r}) - h_b(0)]}, \quad (53)$$

where the external potential, in electrostatic problems generated by permanent charges distributed over surfaces and accounted for by the boundary conditions, is omitted from the expression. Furthermore, we introduce an

electrostatic potential,  $\psi(\mathbf{r})$ , defined as

$$q\psi(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')u(\mathbf{r}, \mathbf{r}'). \quad (54)$$

To transform the OZ-RPA equation in Eq. (14) into desired form, we apply the Laplacian operator to both sides of the equation,

$$\nabla^2 h(\mathbf{r}, \mathbf{r}') = \frac{\beta q^2}{\epsilon} \left[ \delta(\mathbf{r} - \mathbf{r}') + \rho(\mathbf{r})h(\mathbf{r}, \mathbf{r}') \right], \quad (55)$$

where we used the identity

$$\nabla^2 u(\mathbf{r}, \mathbf{r}') = -\left(\frac{q^2}{\epsilon}\right)\delta(\mathbf{r} - \mathbf{r}'). \quad (56)$$

We carry out the same operation on Eq. (54),

$$\epsilon \nabla^2 \psi(\mathbf{r}) = -q\rho(\mathbf{r}), \quad (57)$$

and the result is the standard Poisson equation.

Eq. (53), (55), and (57) constitute the RPA approximation for a density distribution and an electrostatic potential within the RPA level of approximation. Correlational contributions enter through the correlations in the number density  $h(\mathbf{r}, \mathbf{r}')$ . These can be related to correlations in electrostatic potential using a slightly rearranged OZ-RPA equation,

$$\begin{aligned} h(\mathbf{r}, \mathbf{r}') = & \\ -\beta \int d\mathbf{r}'' & \left[ \rho(\mathbf{r}'')h(\mathbf{r}', \mathbf{r}'') + \delta(\mathbf{r}' - \mathbf{r}'') \right] u(\mathbf{r}, \mathbf{r}''). \end{aligned} \quad (58)$$

The term in square brackets,  $\rho(\mathbf{r}'')h(\mathbf{r}'', \mathbf{r}')$ , is identified as a correlation hole generated by a fixed particle at  $\mathbf{r}'$  and the delta function denotes the density of a fixed particle. The integral on the right hand side can be reinterpreted as a perturbation of an electrostatic potential,  $\Psi(\mathbf{r}, \mathbf{r}')$ , caused by a fixed particle at  $\mathbf{r}'$  (the total electrostatic potential is  $\psi(\mathbf{r}) + \Psi(\mathbf{r}, \mathbf{r}')$ ). The OZ-RPA equation simply becomes

$$h(\mathbf{r}, \mathbf{r}') = -\beta q \Psi(\mathbf{r}, \mathbf{r}'), \quad (59)$$

and the proportionality between the two fluctuating quantities is established. Note that this is not an exact equality but a result specific of the RPA approximation.

For a concrete example we consider a counterion only system confined to a half-space  $x > 0$ . The counterion charge is  $q = e$ . The wall surface charge  $\sigma_c$  at  $x = 0$  assures neutrality of the system. The dielectric constant is the same on both sides of the wall. As the bulk density far away from the wall vanishes, the contact density is determined solely by the surface charge (not the pressure),

$$\rho(0) = -\int_0^\infty dz \rho(z) \frac{\partial U(z)}{\partial z} = \frac{\beta \sigma_c^2}{2\epsilon}, \quad (60)$$

where  $-\partial U(z)/\partial z = -e\sigma_c/2$  is a constant force felt by particles on account of a uniform wall charge. The mean-field solution to this problem is

$$\rho_{\text{mf}}(x) = \frac{\beta \sigma_c^2}{2\epsilon} \left[ \frac{1}{1 + \beta q \sigma_c x / 2\epsilon} \right]^2, \quad (61)$$

and it captures a weakly correlated limit. On the opposite end is the strong-coupling limit [31, 32],

$$\rho_{\text{sc}}(x) = \frac{\beta \sigma_c^2}{2\epsilon} e^{-\beta q \sigma_c x / 2\epsilon}. \quad (62)$$

As correlations become significant, the density evolves from one functional form to another,  $\rho_{\text{mf}} \rightarrow \rho_{\text{sc}}$ . A perturbative Gaussian approach for a counterion-only system yields a semi-analytic expression for a density correction  $\Delta\rho(z)$ ,  $\rho(z) = \rho_{\text{mf}}(z) + \Delta\rho(z)$  [22, 33], where  $\int_0^\infty dz \Delta\rho(z) = 0$ , to maintain neutrality, and  $\Delta\rho(0) = 0$ , not to violate the contact value theorem. The corrected density develops a "hump" at a short distance from a wall. It is difficult to justify or trace the hump to a physical cause as it is not confirmed by simulations; simulations always yield a non-monotonic density profile. It should be concluded that the evolution of the "hump" is an artifact of the approximation. It is hoped that the self-consistent equations of the RPA method eliminate the "hump" in iterative steps and in closer agreement with the true system. Our computations, however, indicate that self-consistency only slightly alters the results of the perturbative approach (see Fig. 4). The conclu-

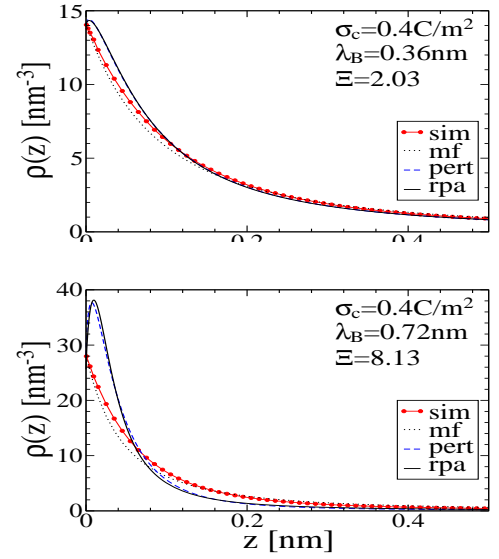


FIG. 4: Counterion density profiles for a counterion-only wall model.  $\Xi$  denotes the coupling constant corresponding to the ratio of the Bjerrum and the Gouy-Chapman length,  $\lambda_B$  and  $1/(2\pi\lambda_B\sigma_c)$ , respectively. The larger the  $\Xi$ , the more significant the correlations.

sion is that the RPA approximation is not very accurate for the counterion-only system, and modifies the perturbative results only negligibly.

## VII. ELECTROLYTE

Continuing with electrostatics, we move toward electrolytes. We consider a symmetric electrolyte,  $q : q$ , with a bulk concentration of both species  $\rho_b$ . The two types of pair interactions are

$$u_{kl}(\mathbf{r}, \mathbf{r}') = \begin{cases} u(\mathbf{r}, \mathbf{r}') & \text{if } k = l \\ -u(\mathbf{r}, \mathbf{r}') & \text{if } k \neq l, \end{cases}$$

where  $u(\mathbf{r}, \mathbf{r}')$  is the Coulomb potential given in Eq. (52).

For a two species system, there are four different correlation functions,  $h_{kl}(\mathbf{r}, \mathbf{r}')$ . Within the RPA they can be expressed in terms of a single function. Accordingly, we have

$$h_{kl}(\mathbf{r}, \mathbf{r}') = \begin{cases} h(\mathbf{r}, \mathbf{r}') & \text{if } k = l \\ -h(\mathbf{r}, \mathbf{r}') & \text{if } k \neq l \end{cases}$$

and  $h(\mathbf{r}, \mathbf{r}')$  is obtained from the OZ-RPA relation,

$$\begin{aligned} h(\mathbf{r}, \mathbf{r}') = & \\ -\beta \int d\mathbf{r}'' \left[ \rho(\mathbf{r}'') h(\mathbf{r}', \mathbf{r}'') + \delta(\mathbf{r}' - \mathbf{r}'') \right] u(\mathbf{r}, \mathbf{r}''), \end{aligned} \quad (63)$$

where  $\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$  is the total density. Within the RPA, the number density of each species is

$$\rho_{\pm}(\mathbf{r}) = \rho_b e^{\mp \beta q \psi(\mathbf{r})} e^{\frac{1}{2} [h(\mathbf{r}, \mathbf{r}) - h_b(0)]}, \quad (64)$$

where the correlation function is obtained from a transformed Eq. (63) (by applying the Laplacian operator to both sides of the OZ-RPA equation),

$$\epsilon \nabla^2 h(\mathbf{r}, \mathbf{r}') = \beta q^2 \left[ \rho(\mathbf{r}) h(\mathbf{r}, \mathbf{r}') + \delta(\mathbf{r} - \mathbf{r}') \right]. \quad (65)$$

Together with the Poisson equation,

$$\epsilon \nabla^2 \psi(\mathbf{r}) = -\rho_c(\mathbf{r}), \quad (66)$$

where  $\rho_c(\mathbf{r}) = q\rho_+(\mathbf{r}) - q\rho_-(\mathbf{r})$  is a charge density, we have a complete approximation for a density and electrostatic potential of a symmetric electrolyte.

As in the case of a one-component plasma, we may link the correlations in a number density to the correlations in an electrostatic potential. We identify the term in brackets in Eq. (63) as a charge correlation hole generated by fixing either a positive or a negative charge  $q$  at  $\mathbf{r}'$ . For a fixed positive charge we have

$$\begin{aligned} \rho_{\text{hole}}(\mathbf{r}, \mathbf{r}') &= \rho_+(\mathbf{r}) h_{++}(\mathbf{r}, \mathbf{r}') - \rho_-(\mathbf{r}) h_{+-}(\mathbf{r}, \mathbf{r}') \\ &= \rho_+(\mathbf{r}) h(\mathbf{r}, \mathbf{r}') + \rho_-(\mathbf{r}) h(\mathbf{r}, \mathbf{r}') \\ &= \rho(\mathbf{r}) h(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (67)$$

Consequently, the fluctuations in the number density are proportional to the fluctuations in electrostatic potential,

$$h(\mathbf{r}, \mathbf{r}') = -\beta q \Psi(\mathbf{r}, \mathbf{r}'), \quad (68)$$

as was previously demonstrated for a one-component plasma in Eq. (59).

Note that the excess chemical potential does not include the mean-field contributions and depends exclusively on correlations,

$$\mu_{\text{ex}}^{\pm} = -\frac{1}{2} \lim_{r \rightarrow 0} \left[ k_B T h_b(r) + u(r) \right]. \quad (69)$$

The mean-field contributions cancel out by virtue of charge neutrality. The same is true of pressure which reads

$$P_{\text{ex}} = -\frac{k_B T \rho_b}{2} \lim_{r \rightarrow 0} \left[ h_b(r) - \int_0^1 d\lambda \frac{h_b^{\lambda}(r)}{\lambda} \right], \quad (70)$$

and where  $\rho_b = \rho_+^b + \rho_-^b$  is the bulk total density.

For bulk electrolytes Eq. (65) recovers the Debye-Hückel theory for a point-charge,

$$\frac{d^2 h_{\lambda}^b(r)}{dr^2} = \kappa_{\lambda}^2 h_{\lambda}^b(r) + \left( \frac{\lambda \beta q^2}{\epsilon} \right) \delta(r). \quad (71)$$

where  $\kappa_{\lambda} = \sqrt{\lambda \beta q^2 \rho_b / \epsilon}$  is the screening parameter. The Debye-Hückel solution is

$$h_b^{\lambda}(r) = -\frac{\lambda \beta q^2 e^{-\kappa_{\lambda} r}}{4\pi \epsilon r}, \quad (72)$$

and the excess pressure becomes

$$\begin{aligned} P_{\text{ex}} &= \frac{q^2 \rho_b}{8\pi \epsilon} \lim_{r \rightarrow 0} \left[ \frac{e^{-\kappa r}}{r} - \int_0^1 d\lambda \frac{e^{-\kappa_{\lambda} r}}{r} \right] \\ &= -\frac{\kappa}{3} \frac{q^2 \rho_b}{8\pi \epsilon} \end{aligned} \quad (73)$$

where  $\kappa \equiv \kappa_{\lambda=1}$ . The total pressure may be written as [34]

$$\beta P = \rho_b - \frac{\kappa^3}{24\pi}. \quad (74)$$

We note that the RPA correlations reduce the ideal gas pressure. From the contact value theorem we may infer that at neutral interfaces the contact density will be lower than that in a bulk, indicating a depletion zone that is not caused by dielectric discontinuity but a more efficient bonding arrangement within a bulk.

Once again resort to a simple wall geometry for testing purposes. The wall is uncharged and its only function is to create an interface between an electrolyte and an empty space. Dielectric constant is uniform across the interface and everywhere else. The results in Fig. (5) indicate the depletion zone near an interface, neither caused by dielectric discontinuity nor finite ion size but correlations. The repulsion of ions from an interface in turn increases the surface tension [35]. As for the two component GCM in Fig. (3) this is caused by a more efficient salvation of ions in a bulk, where each ion is accompanied by an opposite charge-cloud. Near the interface, the charge-cloud is deformed by a nearby interface rising the cost of an energy.



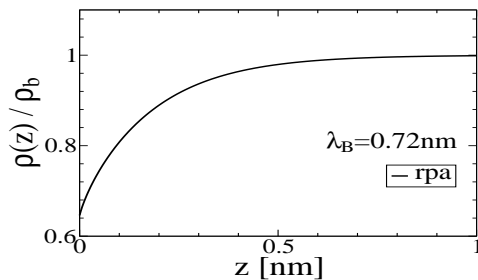


FIG. 5: Density profiles for a 1:1 electrolyte near a wall at  $z = 0$ . The Bjerrum and the screening lengths are  $\lambda_B = 0.72$  nm and  $\kappa^{-1} = 0.33$  nm, respectively. The ions are depleted from a wall region to minimize the number of particles at an interface.

### VIII. CONCLUSION

The free energy formulation using the adiabatic connection offers a simple way for incorporating the OZ equation into a theoretical framework for liquids and may be considered as an extension of the integral equation theories to inhomogeneous fluids. Finally, the choice of closure determines an approximation. In the present work we explore the RPA closure,  $c_\lambda(\mathbf{r}, \mathbf{r}') = -\lambda\beta u(\mathbf{r}, \mathbf{r}')$ . We demonstrate that the resulting general RPA approximation is equivalent to the field-theoretical variational Gaussian approximation, derived completely within the liquid-state theory.

We test the developed RPA framework for different inhomogeneous fluids for a simple wall geometry. For the Gaussian core model the RPA density profiles show decisive improvement over the mean-field and are in good agreement with a simulation, even for large interaction strengths. For the counterion-only system the RPA is

less accurate. Like the perturbative Gaussian approximation [22, 33] the density profile develops an unphysical bump near the wall. In comparison, the simulated profiles are always monotonically decreasing. Furthermore, the self-consistency of our approach appears to modify rather negligibly the profile obtained from the perturbative scheme [22, 33]. Consequently, we conclude that the RPA (or the variational Gaussian approximation) is not an accurate theoretical tool for strongly correlated Coulomb fluids. Finally, we test apply the RPA to a symmetric electrolyte near a neutral interface, without dielectric discontinuity. We observe the depletion of density near an interface generated exclusively by correlations, since the mean-field contributions in this system are cancelled out.

As final remarks, we restate that we did not see that the self-consistent scheme of the RPA (or the variational Gaussian) produces significant modifications in comparison with the results obtained perturbatively. If there are situations where self-consistency is crucial, we cannot be sure, but for systems and parameters considered in this work we did not come across such conditions. Finally, as the future project, we think it worthwhile to explore the adiabatic connection framework presented in this work but for more accurate closures. Self-consistency in these more advanced closures may turn out to be more significant.

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